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SECOND QUARTERLY REPORT
FOR

THE IMPROVEMENT OF ZINC ELECTRODES FOR ELECTROCHEMICAL CELLS
(13 September 1964 - 12 December 1964)

CONTRACT NO. : NAS5-3908

Prepared by:

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GODDARD SPACE FLIGHT CENTER

Greenbelt, Maryland

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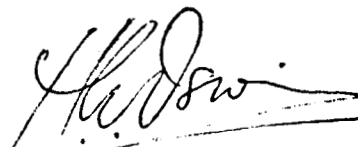
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ABSTRACT

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The E - i characteristics of the $\text{Zn}/\text{Zn}(\text{OH})_4^{2-}/\text{KOH}$ system have been characterized further using rapid, controlled-potential sweeps. The data is in agreement with the previous data and supports the existence of a passive region. The thin oxide layers produced were capable of reduction at extremely high current densities.

Metallographic cross-sections of dendrite growths show no relationship between nucleation sites and grain-orientation or grain-boundaries. The large number of slip plane defects observed may be a contributing factor. One cross-section clearly shows that only a small proportion of nucleated dendrites propagate to significant dimensions when charged under diffusion-limited conditions.

The rate of propagation of dendrites was measured in terms of mm/coulomb. It was shown that rate of growth increases with increasing overpotential. Recharging on partially discharged dendrites appears to promote densification. Two new forms of dendrite were observed. Preferred propagation at the edges of electrodes was observed and an explanation of this is offered and the practical implications discussed.

The importance of zincate-diffusion as a controlling factor in propagation of dendrites is discussed. Some possible effects of anion complexation are also discussed. Factors governing the penetration of separators are considered together with some probable requirements of the separator envelopes.

A program for the next period covers the initial investigation of some possible remedies, observation of dendrite densification on cycling and some preliminary kinetic studies.

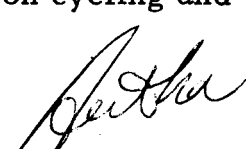


TABLE OF CONTENTS

<u>Section</u>		<u>Page</u>
	Abstract	ii
I	Introduction	1
II	Experimental	4
2. 1	Experimental Methods	4
2. 2	Experimental Results	6
2. 3	Discussion of Data	17
2. 4	New Technology	25
III	Program for the Next Reporting Period	26
IV	Conclusions and Recommendations	27

LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Fast Potential Sweeps on Zn Electrodes in 44(w)% KOH (Sweep rate: 120 mV/sec)	6
2	Etched Polycrystalline Zinc Electrode	8
3	Cross Section of Mossy Dendrites Grown on Poly- crystalline Zinc at -1725 mV, etched, in polarized light	8
4	Cross Section of Pine-Tree Dendrites Grown on Poly- crystalline Zinc at -1850 mV, etched, in polarized light	9
5	Cross Section of Acicular Dendrites Grown on Poly- crystalline Zinc at -1975 mV, etched, in polarized light	9
6	New Dendrite Morphologies Observed During Second Quarter	11
7	Propagation Rate of Dendrite Deposits at Various Potentials	13
8	Current-Time Curves Recorded in Some Experiments of Figure 7	15
9	Effects of Partial Discharge and Regrowth on Propagation at -1700 mV	16
10	Comparison of Linear and Spherical Diffusion Processes	18

SECTION I - INTRODUCTION

Work carried out during the first quarter of the contract was directed towards establishing a qualitative description of zinc-dendrite formations, and some of the growth-controlling factors. The nature of the dendrites was shown to be dependent on the electrode potential (a prime parameter). The more negative (cathodic) the charging potential, the more needle-like the nature of the dendrite and hence the greater the probability of bridging and shorting out the cell. The form of the dendrites was found to be invariant over the normal working range of KOH (30-44 (w)%) and rate of growth, as measured by the current at fixed potentials, was found to be dependent on zincate concentration indicating that a 'limiting-current' condition exists with respect to the zincate species or some secondary species intermediate between zincate and zinc. Some concurrent observations of the potential-current relationships were made for charge and discharge cycles. No studies were made of the effect of separators on dendrite growth: this aspect is being studied in a parallel program by the Yardney Electric Corporation.

In the second quarter, a major objective of the work has been to determine the rates of growth of the dendritic forms as a function of potential and the amount of zinc deposited (i. e., the extent of recharge). This data is required for two reasons - (1) to determine whether the rate of growth (and hence the tendency to bridge) increases with decreasing potential (i. e., increasing rate of charge) and (2) to establish a quantitative yardstick which can be used to measure the effectiveness of methods of suppressing dendritic growth. This second reason is particularly important since the main objective of the work is either to suppress dendrite growth or prevent it from contacting the positive plate. The rate of advance of a dendritic growth therefore becomes a prime measured parameter in any program investigating methods of suppression.

Previously, all studies have been conducted on smooth zinc plates and during this quarter some work was conducted to determine whether the use of such a model electrode is justified. Studies were made, therefore, on zinc plates supplied to us by the Yardney Electric Corporation to determine whether the same types of dendrite are formed on high-area plates and whether the same general dependence on potential is observed.

Although, if time allowed, it would be logical to extend this investigation to an extensive study of the rate of dendrite growth on the high-area electrode, it is believed that such studies, if needed, should be carried out at a later date. This would be done in a phase specifically designed to establish rates of dendrite growth as a function of the composition,

capacity, porosity and mode of preparation of the negative plate. Certainly it can be expected that rates of nucleation and perhaps propagation (in the early growth stages) are dependent on some of the parameters listed above.

In the previous report, an anodic "peak" was reported about 200 mV above the reversible potential. Since a slow potential sweep was used in these studies, the peak could have been attributed either to true passivity or to an increased electrode area being formed during the cathodic cycle. Experiments were conducted in the second quarter using fast potential sweeps to answer this question.

Although a theory (Proc. Roy. Soc. A268:485, 1962) has been proposed for the propagation of dendrites, which invokes diffusion-limited conditions, this theory does not explain, in its simple form, the various dendrite morphologies observed. This theory can explain the propagation of dendrites perpendicular to the plane of the electrode: it does not explain the side-branching observed, nor does it explain the nucleation of dendrites on a smooth surface. These two phenomena may be related, however, and therefore some studies were conducted in an attempt to relate the grain-structure of the zinc substrate to the sites of dendrite nucleation. The results of this investigation indicate that nucleation sites are not associated with grain boundaries and are probably associated with smaller scale imperfections in the surface, such as lattice defects or slip-planes.

The selection of technically sound methods for suppressing dendrite growth can only be as good as our understanding of the basic phenomena: nucleation and propagation. Little can be said about the nucleation process at the moment, though it will be obvious that a high-area plate must be capable of providing a very large number of nucleation sites. Any attempt to interfere extensively with the number of nucleation sites might result in a low-area surface on recharging: such low-area surfaces would have limited discharge rates (because of passivation) and typically a bright surface could not be expected to sustain high rates of discharge. The problem probably resolves, therefore, into tolerating a weak dendritic growth, e. g., the "mossy type" but being able to control the propagation of this type so that growth occurs evenly and without the formation of "bridging spikes" or areas of excessive densification. Some consideration has been given, therefore, to the roles of diffusion, electrode potential and the complexation of the zinc in an attempt to establish a rational basis for the selection of control methods to be evaluated.

At the end of the last reporting period it was proposed that temperature would be varied in a series of experiments. It was later decided that

this information would not be too valuable at this stage. Temperature will affect both rates of diffusion and the rates of the process: $2e + \text{Zn}(\text{OH})_4^{2-} \longrightarrow \text{Zn} + 4 \text{OH}^-$ and will probably not provide by itself any measure of the relative importance of diffusion and electrode potential. From a practical point of view, although increasing temperature will probably tend to diminish dendrite propagation rates, it can hardly be regarded as a practical solution in view of the adverse effect to be expected on the separator materials and the positive plate. No work has been scheduled, therefore, involving temperature as a variable.

A detailed account of techniques and data obtained is now given followed by a discussion of the data, and some interpretations of the more important results.

SECTION II - EXPERIMENTAL

2.1 EXPERIMENTAL METHODS

2.1.1 Materials

In Section 2.1.1 of the first quarterly report, the source and purity of the materials employed, i. e., ZnO, Zn and KOH, were reported. The same materials have been used during this reporting period. In addition, some experiments have been carried out using commercial zinc battery electrodes, provided by the Yardney Corporation. The latter were prepared from rolled electrolytically deposited (dendritic) zinc, and were amalgamated with 1.5 (w)% mercury.

2.1.2 Equipment and Apparatus

2.1.2.1 Cell

A new improved cell has been constructed for the observation of dendrite growth. The main body of the cell was machined from a block of DuPont TFE fluorocarbon resin "Teflon", with a viewing window of optically flat polystyrene. The top was also made from polystyrene and was provided with ports for the positioning of the electrodes, a thermometer and a gas bubbler. Potentiostatic current/time data were recorded using a modified X-Y recorder (Houston Instruments).

2.1.2.2 Current/Voltages Curves

During the first quarter, current/voltage curves were obtained at only one voltage sweep rate (36 mV/min). At such low sweep rates where a complete cycle (2 V, forward and reverse) requires nearly two hours, the zinc substrate undergoes extensive alteration during the course of the sweep. In particular, the electrode area changes continuously due to dendrite formation or dissolution which precludes, in this case, an accurate interpretation of the current/voltage curve in terms of charge or current density. During this reporting period some experiments have been carried out using much faster sweep rates (120 mV/sec) where the time for a complete forward and reverse sweep is reduced by a factor of about 250 (to 10 seconds). When such short sweep times are employed because of the small charge transferred, the

surface area can be regarded as nearly constant for the duration of a single sweep. The fast triangular sweep controlled-potential method, as it is generally termed, was developed by Will and Knorr (Z. Elektrochem. 64, 258, 270 (1960)). In the present arrangement a Wenking potentiostat is driven by a low frequency function generator (Hewlett Packard, 202) such that a triangular voltage/time characteristic is imposed on the working electrode. Current/voltage curves are recorded using a double-beam Tektronix oscilloscope (502). Voltage sweep rates in the range 0.4 V/sec to 400 V/sec are obtainable. The triangular sweep can either be repeated continuously or triggered manually.

The cell for the work reported here was of the conventional H-type with separate compartments for working, counter and reference electrodes. The working electrode (sheet zinc) was sealed in "Scotch-Cast" epoxy and had an area of $9 \times 10^{-3} \text{ cm}^2$. The counter electrode was a large platinized platinum gauze. The reference electrode was a bubbling hydrogen electrode. A Luggin capillary from the reference compartment was positioned close to the working electrode.

2. 1. 2. 3 Dendrite Propagation Rate Measurements

Propagation studies were carried out in 44(w)% KOH saturated with zincate. The rate of dendrite propagation was determined at increments of 25 mV between -1625 and -1975 mV vs. S. C. E. At each potential the current was recorded as a function of time; at intervals a photograph was taken of the deposit and compared with a standard grid. In this way the extent of propagation was determined as a function of the charge passed. The same section of the electrode surface was observed throughout a given growth. The maximum height of the dendrites was taken arbitrarily as the extent of propagation. Between each growth the dendrites were completely removed by anodization at -1400 mV; however, a few experiments were performed in which dendrites were regrown on top of a partially removed deposit. In these experiments the amount removed, in coulombs, was determined from a current/time curve, just as during deposition.

2. 1. 2. 4 Metallographic Cross Section Analysis of Dendrite Nuclei

Zinc discs were cast in epoxy and ground down to expose the zinc on one face. The faces were etched in HCl to expose the polycrystalline structure of the metal and dendrites were grown at various potentials on the etched faces. Each electrode with its dendritic deposit was then vacuum impregnated with epoxy, and cut to expose the substrate and dendrites in cross section. These cross sections were polished with a

series of metallographic papers and finally etched in chromic acid/potassium sulfate for microscopic examination. Both polarized and unpolarized white illumination were employed.

2.2 EXPERIMENTAL RESULTS

2.2.1 Fast Potential Sweep Studies on $\text{Zn}/\text{Zn}(\text{OH})_4^{2-}/\text{KOH}$ System

Figures 1a and 1b show current/voltage curves obtained with the fast potential sweep method. Figure 1a (at 120 mV/sec) was obtained in the absence of dissolved zincate. Figure 1b (at 120 mV/sec) was obtained in the saturated zincate solution. The voltage sweep was from -1800 to -600 mV vs. S. C. E. and back again. The general characteristics of the anodic section of the waves are essentially the same as those found using the slow sweep method (see Quarterly Report No. 1, Figure 5). It was found that in the presence of zincate the magnitude of the peak which occurs when sweeping in the anodic direction is governed by the length of time which the electrode is held at cathodic potentials. This partially confirms a statement made in the first quarterly report (page 13). It should, however, be emphasized that the presence of the peak itself is independent of the formation of dendrites and indicates the onset of passivity.

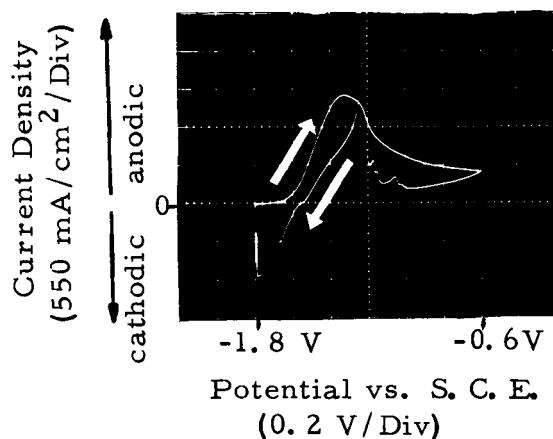


Figure 1a. Zincate-free

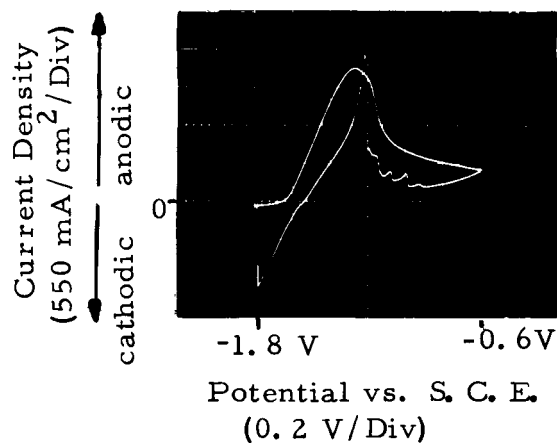
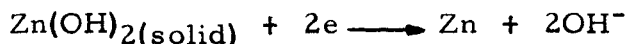


Figure 1b. Zincate-saturated

Fast Potential Sweeps on Zn Electrode in 44(w)% KOH
(Sweep rate: 120 mV/sec)

Some differences were apparent on the cathodic section of the curves that can be attributed to the fast sweep rate. On the return section of the sweep very high cathodic currents were found - up to 1 Amp/cm². This probably results from the reduction of a solid layer of Zn(OH)₂ that is formed during the anodic sweep and which remained attached to the surface of the electrode. The reversible potential for this process,



is seen from Figure 1 to be -1.55 V. This value, which is less cathodic than that obtained using slow sweep rates, is taken from the point where the wave crosses the zero current axis. The latter is clearly marked by an inflection which is characteristic of redox processes.

After all the Zn(OH)₂ has been reduced in Figure 1b the current falls to a value at -1.8 V around 50 - 60 mA/cm² which corresponds to the reduction of zincate from the solution phase.

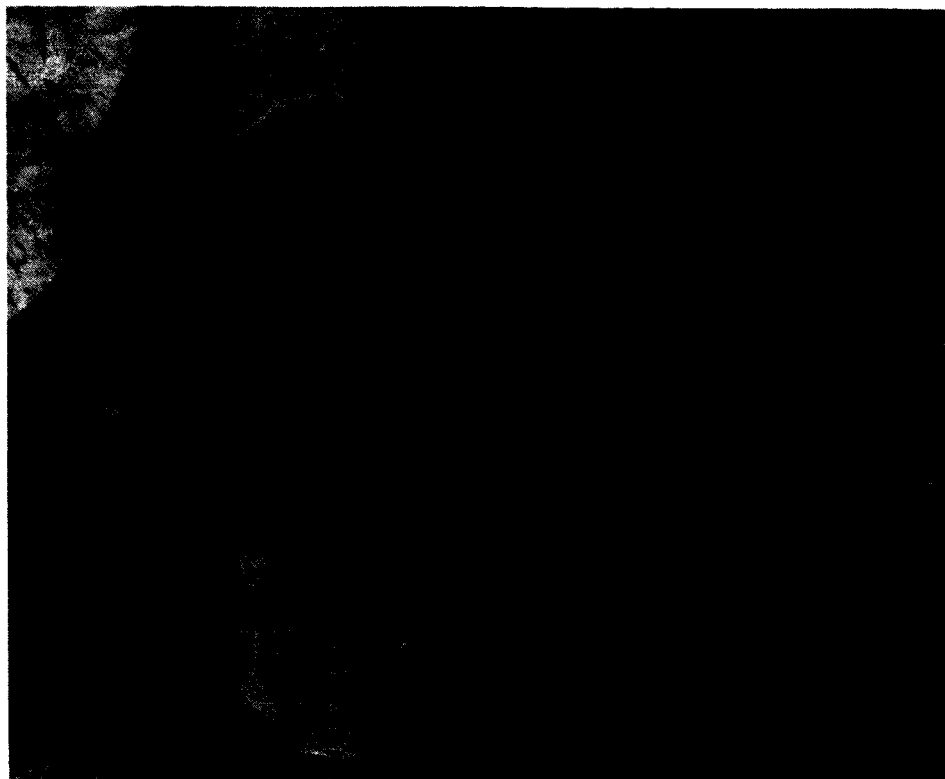
Perhaps the most remarkable aspects of these experiments are the extremely high anodic and cathodic currents recorded (> 1 A/cm²) for a smooth electrode. This points out the limitations imposed on the electrode under normal operating conditions by zincate diffusion control and/or the passivating effect of thicker oxide layers.

2. 2. 2 Metallographic Cross Section Studies of Dendrite Nucleation Sites

Samples of each of the three major types of dendrites were grown at appropriate potentials (as given on each figure) from zincate-saturated 44(w)% KOH. These deposits were prepared for metallographic examination as described in Section 2. 1. 2. 4. Considerable difficulties were experienced in mounting and sectioning these fragile growths.

Figure 2 shows a section of the polycrystalline surface of a zinc disk similar to those used as substrates for dendrite growth. Grain sizes and boundaries are clearly visible. Grain dimensions typically range from 0.05 cms to 0.005 cms. Examination by unpolarized light does not reveal any of the required detail.

Figures 3, 4 and 5 show mossy, pine-tree and acicular dendrites after etching viewed by polarized light. The disposition of the dendrites across the surfaces is clearly shown, as well as the grain structure of the substrate. In addition, because of low reflectivity of the polarized light from the surface of the epoxy, parts of the structures directly beneath the plane can be seen. In scanning the many samples no relationship was found between grains of particular orientation, or grain boundaries and sites of most profuse growth.



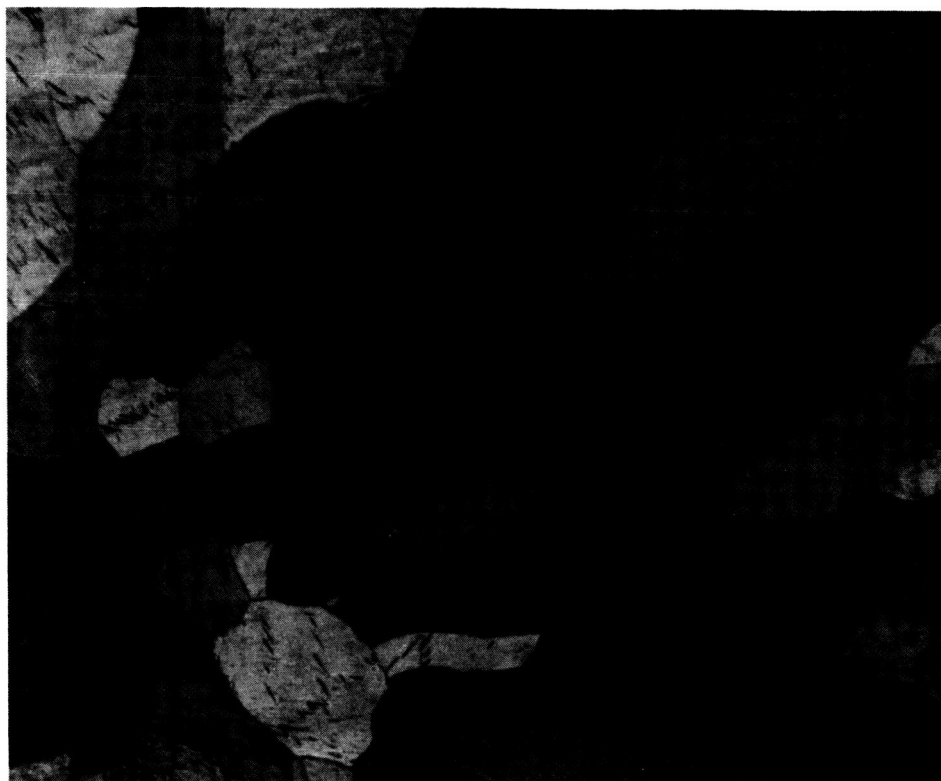
(Mag. 60 X)

Figure 2. Etched Polycrystalline Zinc Electrode in polarized light



(Mag. 60 X)

Figure 3. Cross Section of Mossy Dendrites Grown on Polycrystalline Zinc at -1725 mV, etched, in polarized light



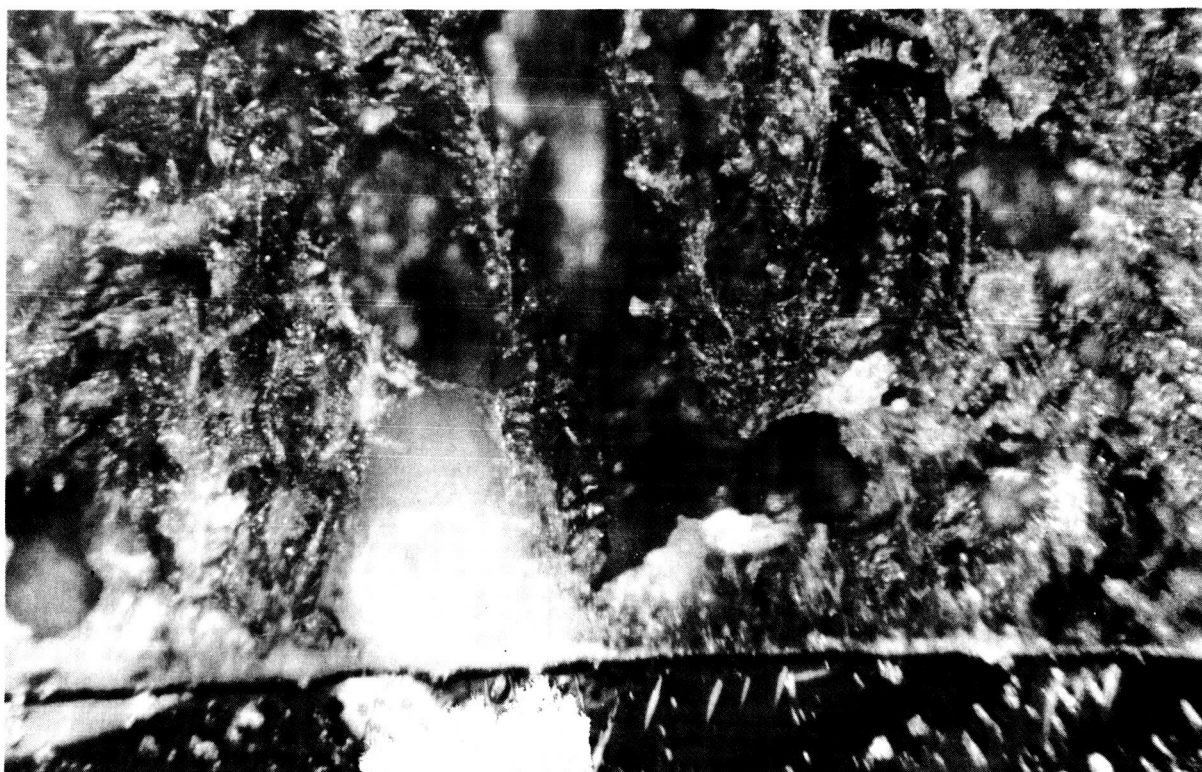
(Mag. 60 X)

Figure 2. Etched Polycrystalline Zinc Electrode in polarized light



(Mag. 60 X)

Figure 3. Cross Section of Mossy Dendrites Grown on Polycrystalline Zinc at -1725 mV, etched, in polarized light



(Mag. 100 X)

Figure 4. Cross Section of Pine-Tree Dendrites Grown on Polycrystalline Zinc at -1850 mV, etched, in polarized light



(Mag. 100 X)

Figure 5. Cross Section of Acicular Dendrites Grown on Polycrystalline Zinc at -1975 mV, etched, in polarized light

The most interesting observation can be made in Figure 5, where it can be seen that many dendrites were nucleated but only a percentage of them grew to size $> .001''$.

This same figure also shows a preferred growth direction perpendicular to the surface which would agree with the requirements of Bockris and Barton for diffusion-controlled propagation.

Figure 2 shows the grain structure of a fresh electrode and is of considerable interest from two points of view. This electrode, prepared by casting from molten zinc shows evidence of dendritic growths in the elongated grain structure which may indicate that the tendency of zinc to form dendrites is inherent in the physical metallurgy of zinc. The second point of interest in this cross section is the larger number of defects apparent on the surface structure. These are probably slip-planes developed by the metallographic treatments although every precaution was taken to minimize "cold working". Zinc is particularly susceptible to such deformation and it may be that these defects are acting as nucleation sites. A quantitative measure of defect sites and nucleation sites would be needed to establish this, but it can be seen that the frequency of defect sites apparent in Figure 2 is not dissimilar from the number of dendrite nuclei shown in Figure 5.

2. 2. 3 Rate of Propagation of Dendrites

Work on this aspect of the program has been done exclusively in 44(w)% KOH saturated with ZnO (about 1.1 M) which approximates the electrolyte conditions of commercial silver-zinc cells. Most of the depositions have been done on substrates of smooth polycrystalline zinc, although some experiments were performed with the commercial zinc electrodes supplied by Yardney and are described above in Section 2. 1. 1.

The object of the work was to determine the rates of propagation of dendrites as a function of the potential of growth (which affects the morphology of the deposit). Secondary questions of interest were whether partial discharge followed by regrowth affects propagation, and whether propagation rates are significantly different on commercial porous electrodes and smooth zinc.

The general trend of morphology with potential noted during the previous reporting period (for the most part in dilute zincate solutions) was still evident in the present work with zincate - saturated electrolyte. There were two additional observations. First, an unbranched dendrite form was observed with some regularity at potentials between approximately -1775 and -1875 mV. An example of this is shown in Figure 6a. The other



(Mag. 100 X)

Figure 6a. Dendrites Grown on Layer-Free Surface at -1775 mV



(Mag. 100 X)

Figure 6b. Dendrites Grown During Reduction of Purple Layer at -1950 mV

observation related to morphology was that at high rates of anodization of zinc in zincate-saturated electrolyte a layer of the oxide (or hydroxide) of appreciable thickness gradually formed on the surface. The layer was at first gray, turning blue, and eventually becoming purple. This phenomenon has been described previously by Dirkse and DeHaan (J. Electrochem. Soc. 105:312 (1958) and by Fry and Whitaker (J. Electrochem. Soc. 106:607 (1959). The coloration is believed to be due to inclusions or stoichiometric excesses of zinc.

When left at open circuit such layers eventually dissolved in the electrolyte, sometimes becoming detached from the zinc substrate before dissolution was complete. On several occasions cathodic deposition of zinc was initiated while the layer was still intact on the surface of the electrode. Large prismatic dendrites, as shown in Figure 6b, characteristically resulted from this procedure. The reason for this is not apparent at the moment.

In the experiments performed with the porous Yardney electrode, the same trend of morphology with potential was found similar to that reported on smooth zinc. The extent of propagation appeared, in general, to be somewhat less, though no data was taken. Preferential growth of dendrites at the edges of the substrate was more marked than with the smooth zinc. This probably has practical significance which is discussed in the next section of the report.

Figure 7 presents typical data on the extent of propagation per coulomb of (cathodic) charge at various potentials of growth. These curves should be taken to indicate approximate behavior of the system since it was found to be impossible to reproduce the results closely from run to run. One reason for this is that with the present equipment and technique only a small portion of the surface is viewed throughout a given growth; in a subsequent growth the field chosen may exhibit a somewhat different growth rate than that of the previous experiment even though, on the average across the entire surface, the extent of growth may be reproduced.

A general characteristic of the curves on Figure 7 is that they exhibit a plateau at which the propagation is independent of the amount of charge. This probably indicates a progressive densification of the deposit. With the exception of the curve at -1950 mV, there is a definite increase of propagation rate with increasing cathodic potential. The apparent deviation of the data at -1950 mV from this pattern may be explainable by the fact that the total number of coulombs passed is the result of two processes: zincate discharge and reduction of water to hydrogen; at -1950 mV the contribution of the latter is appreciable. If it were possible to plot the propagation vs. coulombs of zinc, the trend with potential might hold for all four curves.

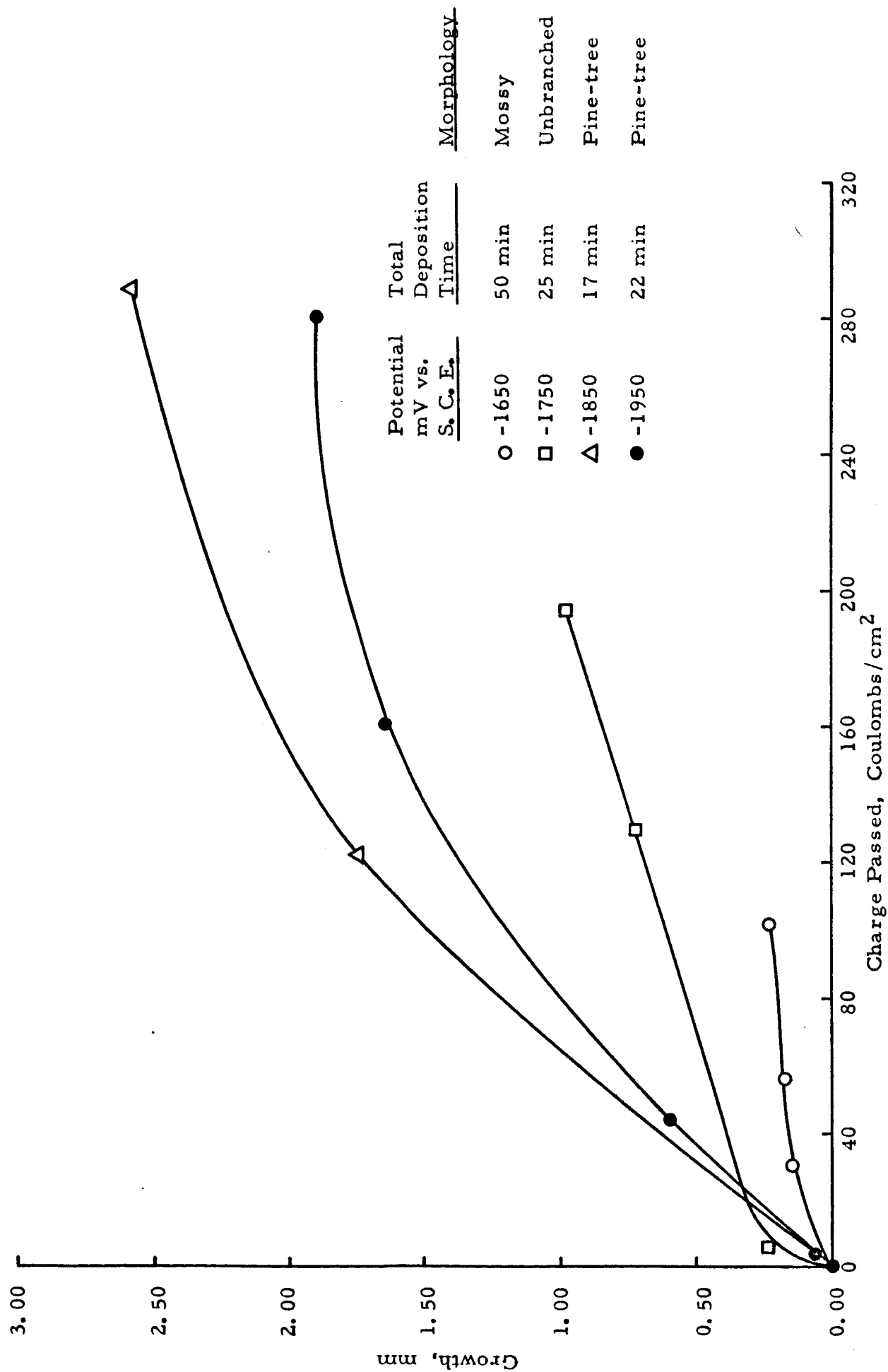


Figure 7. Propagation Rate of Dendrite Deposits at Various Potentials

Figure 8 presents some of the current/time curves recorded for the experiments of Figure 7. The outstanding feature of curve a (-1650 mV; mossy deposit) is the relative constancy of the current with time. This indicates that the deposit grows fairly evenly without large changes in active surface area (confirmed visually by Figure 3). In contrast, curve c of Figure 8 (-1950 mV; pine-tree dendrites) illustrates the current/time relationships of deposition in which active surface area is changing rapidly as deposition continues (the interpretation of this type of curve was discussed in more detail in Quarterly Report No. 1, page 13). The initial high current followed by a rapid drop shortly after polarization is attributed to the establishment of the diffusion gradient of zincate next to the (initially smooth) surface. An exception to the usual rapid drop in this initial current surge is shown in curve b of Figure 8 (-1750 mV; unbranched dendrites). In this case the long slow decrease to a minimum after about nine minutes may be associated with the "anodic" history of the electrode: due to the effects of a previous experiment in which either high local concentrations of zincate, or a film of the oxide remained at the electrode after anodization, thereby providing an abnormal reservoir of ZnO or Zn(OH)_4^{2-} for reduction.

Figure 9 shows the results of a partial anodization followed by regrowth of dendrites grown at -1700 mV. It is seen that the reduction in height during anodization is about proportional to the percentage discharge, and that regrowth does not lead to restoration of the original height until much more zinc is deposited than was removed anodically. From photographs taken during this experiment, it was apparent that anodization created new lateral nucleation sites on which zinc could deposit during regrowth. Thus, the overall effect of the single cycle in this case (and in other experiments at low and moderate overpotentials) was one of densification of the deposit. This result does not help to explain the progressive growth of dendrites in a working cell from anode to cathode during cycling. The extent of propagation during many alternate depositions and anodizations would need to be observed to gain an understanding of the process. It is also possible, of course, that the presence of the separator in the actual cell and the attendant large concentration gradients of zincate are responsible for continued propagation leading to shorts.

In the previous report it was suggested that partial discharge might lead to increased propagation on regrowth because extensive skeletal structures often remained even until the last stages of anodic removal. As explained above, however, this has not been borne out in the experiments on regrowth at potentials down to about -1900 mV. At extremely cathodic potentials (well beyond the usual operating range of commercial cells) some evidence was obtained that this mechanism of propagation induced by cycling could occur.

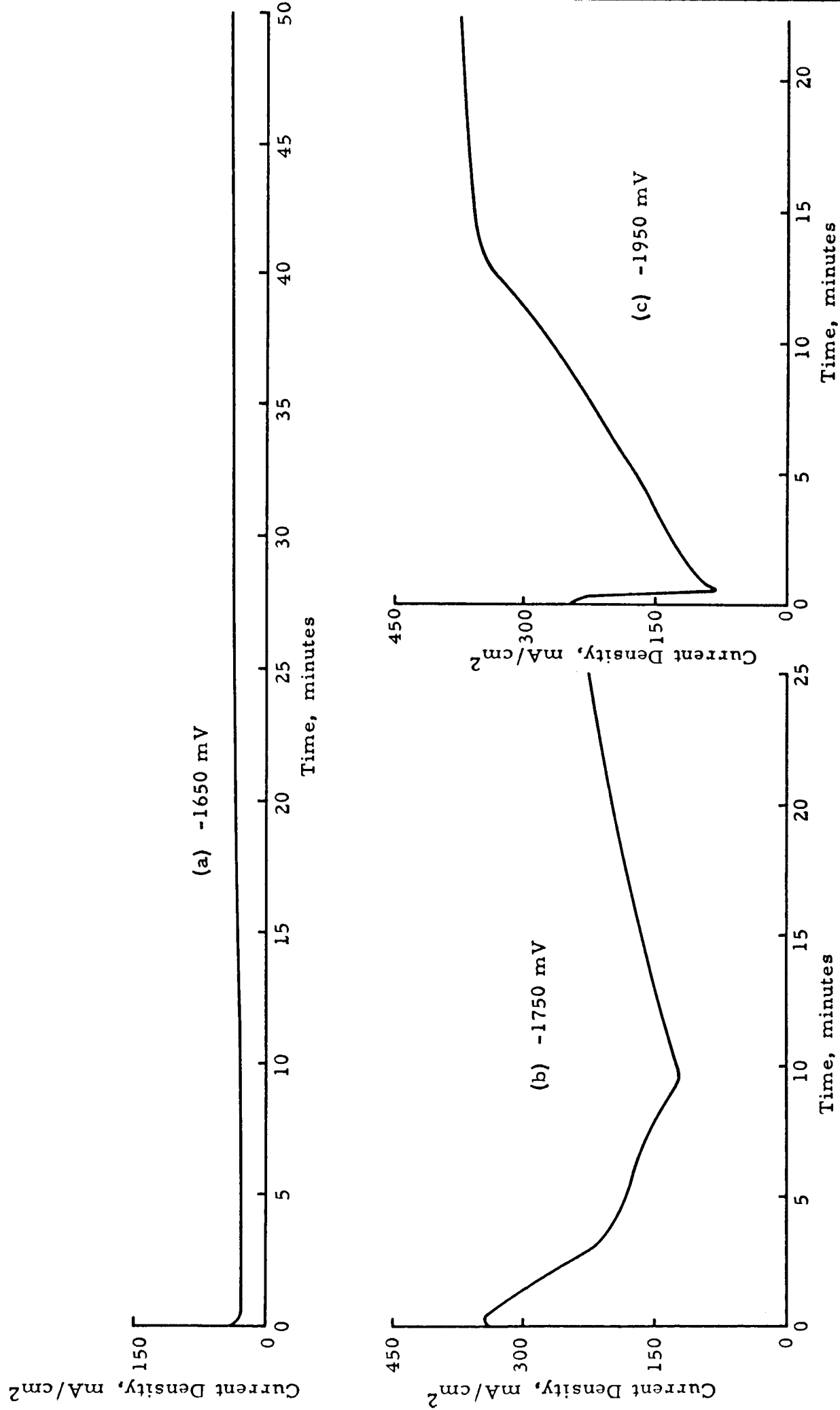


Figure 8. Current-Time Curves Recorded in Some Experiments of Figure 7.

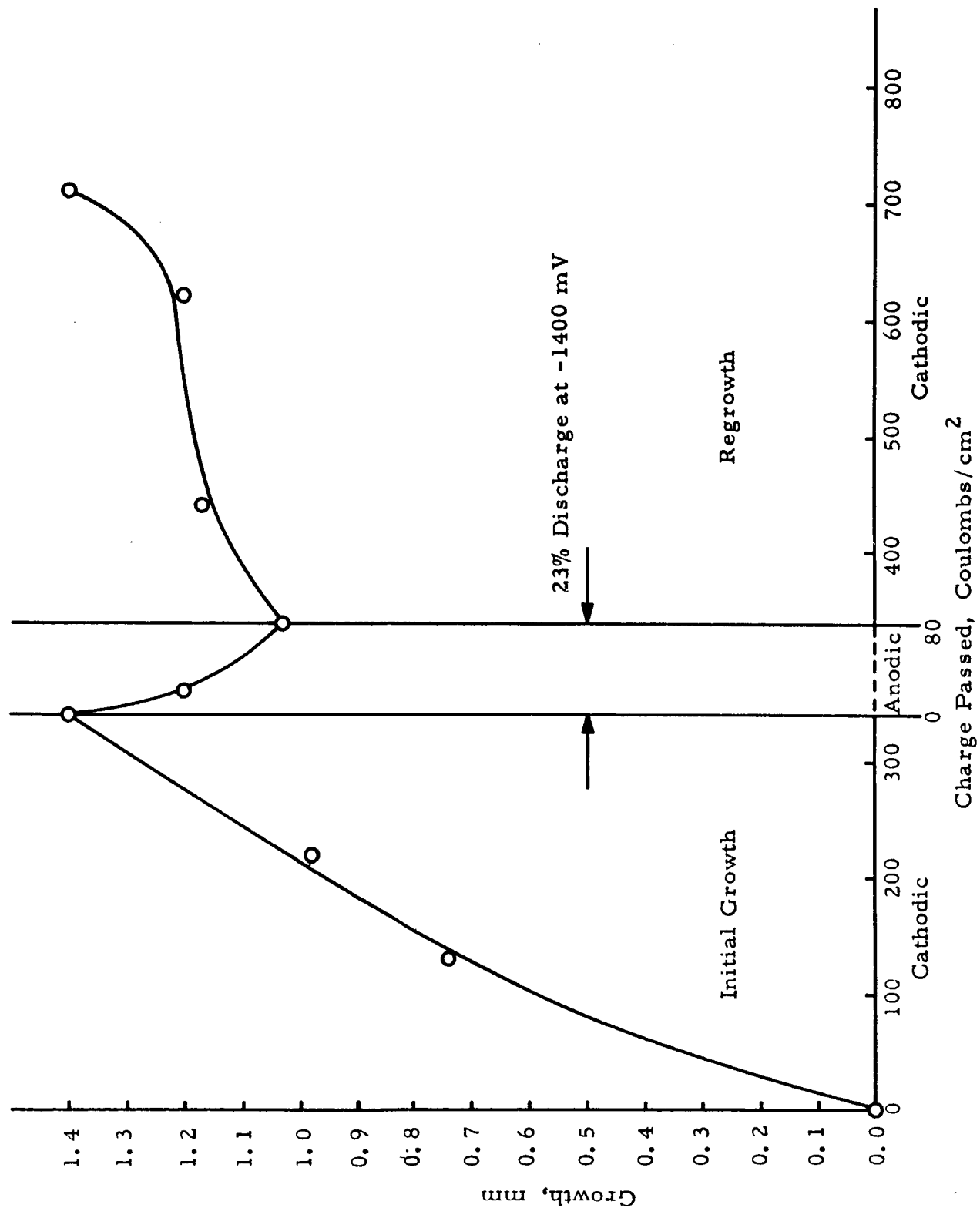


Figure 9. Effects of Partial Discharge and Regrowth on Propagation at -1700 mV

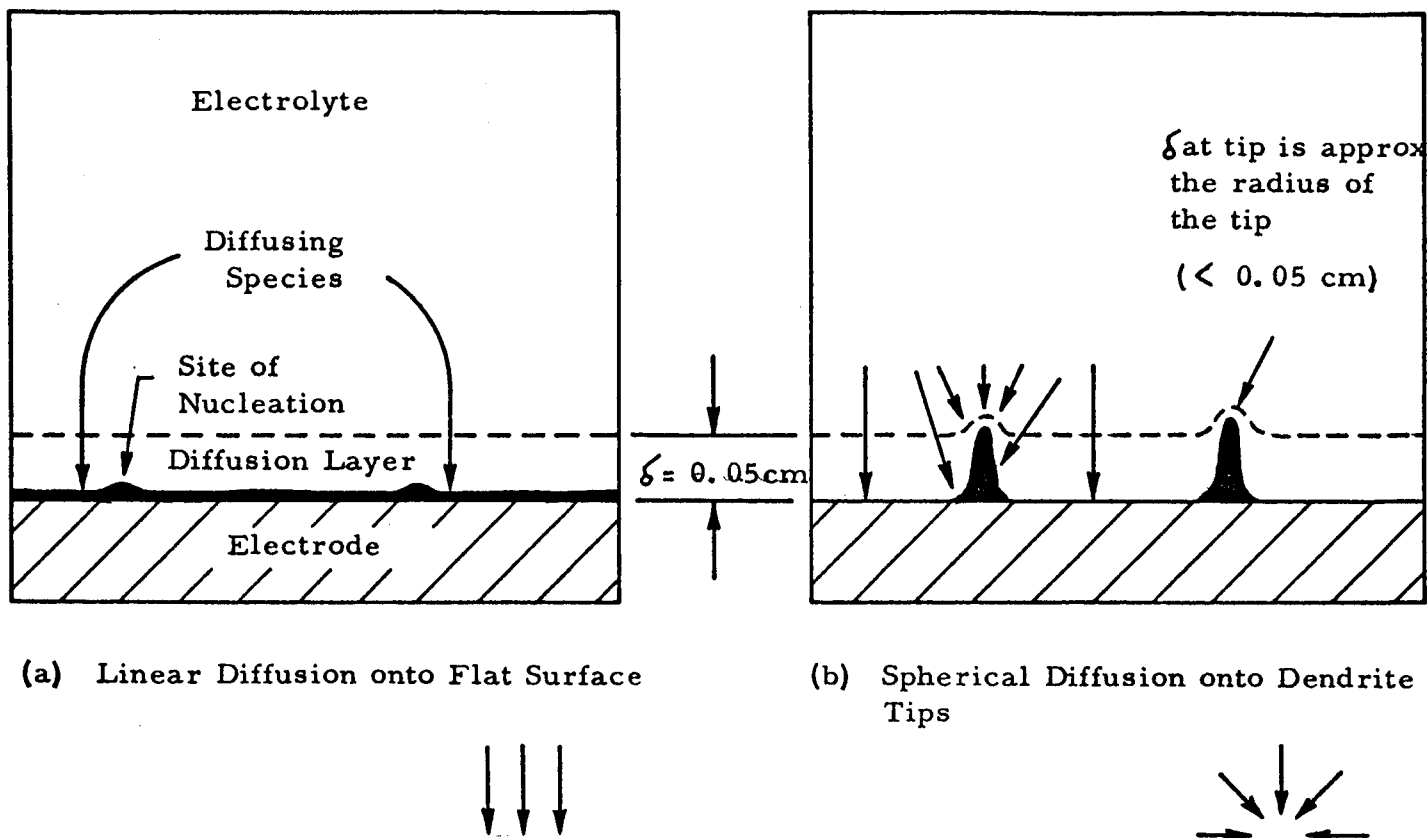
Sufficient evidence has now accumulated to indicate that the diffusion control by the soluble zinc species is an important factor in the propagation of zinc dendrites. The dependence of charging current on stirring (Quarterly Report No. 1, page 12) and the smooth deposit obtained on a rotating electrode (Yardney Electric Corporation Report No. 1, Section 2. 3) both substantiate the importance of diffusion control in dendrite propagation rate.

The results of diffusion control involving the soluble zinc species can be seen clearly in Figure 8c. The current, initially about 240 mA/cm^2 drops rapidly due to the slow diffusion of zinc, reaching a minimum of 90 mA/cm^2 after thirty seconds. At this stage some dendrites penetrate the stagnant, zinc-starved layer of electrolyte adjacent to the electrode and begin to grow rapidly in the zinc-rich, bulk electrolyte. At this point, as the dendrite dimensions increase, the diffusion limitations are reduced and the zinc-limiting current increases, as shown, to a maximum current density of 360 mA/cm^2 after fifteen minutes. The conditions which exist are shown schematically in Figure 10a and b. The portion of the current/time curve Figure 8c from 0 - 30 seconds represents the attainment of the diffusion conditions depicted in Figure 10a - current is limited by linear diffusion of Zn(OH)_4^{2-} in a well-defined boundary layer. Beyond the point of minimum current, however, penetration of the boundary layer has occurred and the 'spherical diffusion' conditions shown in Figure 10b now determine the limiting current. When these latter conditions are attained, the larger dendrites effectively grow at the expense of the smaller dendrites which have failed to grow to boundary-layer dimensions.

It will be noted in Figure 8a that the minimum and maximum of current density (30 and 40 mA/cm^2 respectively) are only slightly different. Under these conditions no excessive penetration of the boundary layer has occurred and a less pronounced dendrite growth (mossy) is observed. Whether Bockris and Barton's theory of dendrite propagation can be applied to the situation where an even, mossy growth is observed, is questionable.

If zincate-diffusion is the cause of dendrite growth, then it should be possible to define a limiting-current condition, above which dendrites form, and below which they do not.

Unfortunately, no data appears to be available on the diffusion coefficient of zincate in concentrated KOH. This is surprising in view of its importance in estimating accurately transport rates in working cells.



Diffusion takes place across a gradient of concentration known as the diffusion layer; its rate is inversely proportional to the thickness of this layer (δ). Hence, deposition at a protrusion of small radius is more rapid than at a flat surface.

Figure 10. Comparison of Linear and Spherical Diffusion Processes

Such information cannot be determined by zincate deposition onto zinc itself because of:

- a. the simultaneous evolution of hydrogen, and
- b. the rapid changes in real surface area of the zinc due to the roughness of the deposits.

Reliable data must be obtained polarographically on the dropping mercury electrode. Initial attempts to do this at LML were unsuccessful because of the appearance of large background currents (presumably due to other constituents of the solution: slight amounts of impurities in the reagent KOH become magnified in effect because of the very high concentration of the electrolyte). Further measurements will be made to establish the Zn(OH)_4^{2-} diffusion coefficient.

For the present, an estimate of the diffusion coefficient can be derived from the data given by Kolthoff and Lingane (Polarography, 2nd Edition, Vol. I, page 63 and Vol. II, page 504; Interscience, New York, 1952). This value is $6.7 \times 10^{-6} \text{ cm}^2/\text{sec}$ in 1N NaOH at 25°C . The viscosity ratio $\frac{\eta(44(\text{w})\% \text{KOH})}{\eta(1\text{N NaOH})}$ is approximately 5. Neglecting possible changes in solvation, the diffusion coefficient is inversely proportional to viscosity and an estimate for the present system based on the above data is $1.3 \times 10^{-6} \text{ cm}^2/\text{sec}$.

The equation for the limiting current due to semi-infinite linear diffusion is:

$$i_d = \frac{nFDC^0}{\delta}$$

where,

- | | | |
|----------|---|--|
| i_d | = | the limiting current density |
| C^0 | = | the concentration of the diffusing species in the bulk of the solution (of the order of 1M for zincate-saturated 44(w)% KOH) |
| δ | = | the diffusion layer thickness (estimated at $5 \times 10^{-2} \text{ cm}$) |

Using the value for D estimated above, the limiting current for the reduction of zincate in 44(w)% KOH saturated with ZnO at ambient temperature

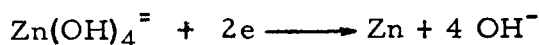
is of the order of 5 mA/cm². As already stated, it is impossible to check this result on the zinc electrode itself; however, attempts will be made to establish a value polarographically.

Thus on the basis of the above calculations, dendrite propagation conditions will be favored at currents > 5 mA/cm². Below 5 mA/cm², dendrite propagation should be less severe.

Looking at the practice of bright-plating zinc from zinc chloride or zinc sulfate solutions, bright plates are obtained at current densities in excess of 100 mA/cm² from approximately 1M Zn⁺⁺ electrolytes. Using data from Kolthoff and Lingane, $D_{Zn^{++}} = 8 \times 10^{-6}$ cm²/sec (N/10 KCl) a limiting current density between 15 and 30 mA/cm² is derived. Yet bright plates of Zn are obtained at current densities considerably higher than this. It seems doubtful, therefore, whether zincate diffusion control alone can explain dendrite formation, and particularly at conditions (5 mA/cm²) where diffusion control is marginal.

We must consider, therefore, whether the electron-transfer process plays an important role in initiating dendrites and in the early propagation stages. This can only be determined from a knowledge of the kinetics of the electrode process(es) which is not presently available. It is important to know:

- a. whether electron transfer takes place directly from zincate

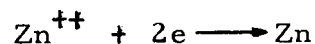
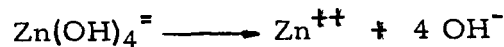


or

- b. from $Zn(OH)_3^{-}\ +\ 2e\ \longrightarrow\ Zn\ +\ 3\ OH^{-}$ (reference Dirkse, Postmus and Vandenbosch, J. Amer. Chem. Soc., 76, 6022 (1954))

or

- c. whether Zn⁺⁺ is an intermediate



(In the latter case, the extremely low (Zn⁺⁺) concentration in 44(w)% KOH would be an important factor in determining the overpotential for deposition via this species.)

- d. If (a) represents the electrode process, how will the concentration of $\text{Zn}(\text{OH})_4^{2-}$ in the double layer vary with electrode potential? This complex anion will tend to be repelled from the electrode surface as the charging potential on the zinc becomes more negative. This would markedly affect overpotential relationships and might tend to enhance deposition rates at the points of lower overpotential. A better understanding of the effects of complexation of the Zn^{++} ion is needed before these questions can be answered.

2. 3. 2 Dendrite Nucleation

Figure 5 shows the extensive nucleation of dendrites on a surface - only a few of these have grown to significant dimensions and have done so clearly at the expense of the small ones which were probably 'zinc-starved'.

It is important to know how and why dendrite formations are initiated and whether the process is controlled by parameters different from those which control propagation. It appears, for example, that the mossy form of dendrites is propagated at current densities where the zincate diffusion should not be limiting. Then we must ask the question; why are these dendritic forms initiated? The preliminary work done on smooth zinc indicates that grain boundaries are an unimportant factor. Thus, the nucleation process must be due to one of the following factors or a combination of them:

- a. The high defect concentration of the zinc lattice;
- b. A low deposition overpotential associated with a specific crystal plane of the zinc;
- c. The current potential relationships governing the discharge of the complex zinc anion.

At this point, it is not possible to select any of the above factors as the sole cause of nucleation. Some orienting studies will be needed to point the direction for further research in this area.

2. 3. 3 Dendrite Growth Through Separator Materials

The studies reported by Yardney Electric Corporation in their First Quarterly Report indicate that propagation rates through the cellophane

are low. It would also appear that growth into the membrane does not take place until the zincate concentration in the liquid electrolyte phase surrounding the zinc plate has diminished to a concentration insufficient to support the imposed charging current. When this condition arises, the electrode overpotential will increase because of the zincate limiting current condition and dendrites will then begin to grow within the cellophane which is now the only source of soluble zinc. When dendrite growth commences within the cellophane, the formation of a solid zinc phase will cause permanent disruption of the cellulose chains. Thus on discharge and dissolution of the zinc within the cellophane small holes are left in the cellulose matrix which can now act as preferred zincate diffusion paths in the next charging cycle. Therefore, once penetration through the cellophane has occurred in successive charging cycles, dendrites will propagate more readily through the tiny holes in the cellophane and the process, when repeated, will lead to continual enlargement of the holes, providing zincate diffusion paths of lower resistance on each cycle. Such a situation must now lead to the eventual propagation of a few dendrites at the points of penetration which will bridge to the positive plate and short out the cell. It would appear, therefore, that once penetration of the cellophane has occurred, eventual shorting between the plates is inevitable, unless the length of the charge cycle is reduced.

The effective resistance to diffusion offered by separator materials is, of course, much higher than that of the free electrolyte. The flux of zincate across 4 mils of cellophane between 44(w)% KOH solutions of 0 and 1M zincate, respectively, has been found to be 1.59×10^{-6} moles/in²/min (J. E. Cooper and A. Fleischer, Characteristics of Separators of Alkaline Silver Oxide-Zinc Secondary Batteries: Screening Methods, page 121; Air Force Aero Propulsion Laboratory, 1964). The value of the apparent (solution-to-solution) diffusion coefficient calculated from this flux is 4.2×10^{-8} cm²/sec; or only about 3% of that in the free electrolyte. Other separator materials yield an even lower value.

One requirement, therefore, to prevent penetration of the cellophane is that the free electrolyte volume surrounding the zinc plate should contain sufficient dissolved zinc to satisfy the "zinc demand" during the charging cycle. In fact, an excess of zinc should be available within the cellophane envelope. If this condition is not satisfied and there is an inadequate reservoir of zincate available within the cellophane envelope, then penetration beyond the envelope will occur at the point where there is a minimum resistance to zincate diffusion. This points out the necessity for wrapping the zinc plate with cellophane in such a way that no open diffusion paths are available for zinc to diffuse from the bulk electrolyte into the cellophane envelope. For example, if the cellophane is folded in

such a way that the zinc plate at one end is exposed directly to the electrolyte, then once the zinc within the envelope has been exhausted, dendrite growth will occur preferentially at this opening. Such edge effects can be extremely important and are discussed in the next section.

2. 3. 4 Edge Effects on Zinc Plates

It has been observed on both smooth zinc electrodes and porous zinc electrodes supplied by Yardney that the rate of dendrite propagation is greater at the edges than in the center of the plate. This is not regarded as an inherent property of the electrode itself, but rather a result of the geometry of the electrode/electrolyte system and the resultant diffusion paths.

In the center of the plate diffusion of zincate takes place in a direction essentially perpendicular to the plane of the electrode. The rate of growth is thus limited by the rate of transfer of the zinc. At the edges of the plate, however, zincate can be supplied to the electrode by the process of spherical diffusion as shown in Figure 10b. In other words, zinc can also diffuse from the electrolyte at the side of the electrode and since this situation will permit a greater flux of electrolyte to the edge of the electrode, the rate of propagation of zinc dendrites will be greater at the edge.

On this basis one might expect shorting to occur first at the edges of the plates since it would be at this point that the dendrites are growing more rapidly. Since in most battery designs the thickness of the electrolyte layer between the edge of the electrode and the case is greater than the separation between the plates, there is an adequate supply of zinc available to promote this "edge effect" and the conditions are such, therefore, as to promote a build-up of dendrites at the edge of the zinc plate more rapidly than in the center of the plate.

To circumvent this effect (if it is observed under operating conditions), the reservoir of electrolyte at the edges of the plate stacks should be eliminated or minimized. This could be achieved by smaller case dimensions or by packing the free space with a non-wettable material such as a hard plastic foam.

In many battery designs there are more anodes than cathodes; thus the end plates in a cell are generally anodes. We can expect a similar effect to take place at the back of these two end anodes and particularly near the edges. This is because we have a reservoir of zincate available at the back of each end anode of a stack. The build-up of dendrites behind the end-anodes could lead eventually to compression of the stack. This situation could be circumvented by insulating the back surface of end-anodes, or using end-cathodes.

Two important observations were made of the formation of densified zinc areas following a charge - discharge cycle. The formation of local high-density zinc regions is clearly undesirable. Such regions, having lower true surface areas will discharge at lower rates than surrounding low-density regions (of higher surface area). It is likely, therefore, that successive cycles will increase the densification and lead to less than average discharge rates in the affected regions. The net effect of this will be to build up a dense protrusion capable of bridging out the plates. This can only happen if penetration of the cellophane has occurred: penetration could occur prior to the densification process or because of the high local mechanical pressures exerted on the cellophane by the dense protrusion.

Evidence from the present work is that such dense areas can be formed by at least two processes:

- a. Recharging onto a partially discharged dendrite structure appears to favor densification as shown by the data in Figure 9. This situation may be alleviated by a more complete discharge of the dendritic structure or close control over the manufacturing procedures to provide uniform structure. Flatness of the plates and parallelism will also affect somewhat the extent of charge and discharge in localized regions of the plates.
- b. Discharging at high rates followed immediately by a recharging step seems to lead to dense dendritic forms typified by Figure 9.

In particular it seems probable that process (a) may be responsible for the formation of the dense nodules which are reported to have been observed on cycled zinc plates taken from failed batteries.

2. 4 NEW TECHNOLOGY

No new methods or techniques have been developed as a result of the studies conducted during this reporting period.

SECTION III - PROGRAM FOR THE NEXT REPORTING PERIOD

Work for the coming period is projected in three areas:

- (1) A preliminary study of possible remedies. In particular, additions to or modifications of the electrolyte and the effects of current reversal during charging.
- (2) Observation of the changes in density and surface protrusions during successive cycles varying depth of discharge.
- (3) Mechanistic studies
 - a. to define $D_{Zn(OH)_4^{2-}}$
 - b. orienting studies to define the relative importance of anion complexation and overpotential, surface defect concentration and the effects of $[KOH]$ in the range where it affects $[Zn(OH)_4^{2-}]$ and $[Zn(OH)_3^-]$

SECTION IV - CONCLUSIONS AND RECOMMENDATIONS

Although zincate-diffusion appears to be a controlling parameter for the rate of propagation of dendrites at current densities $> 5 \text{ mA/cm}^2$, it is by no means certain that it is the only controlling factor. An accurate measure of the zincate diffusion coefficient is needed to establish the value of the limiting current.

The factors controlling nucleation of dendrites are even less defined, some orienting studies are needed to demonstrate the relative importance of lattice defects and the kinetics of discharge of the zinc anion.

Without more detailed knowledge of the mechanisms and kinetics of dendrite nucleation and propagation, possible solutions to the problem can only be selected somewhat arbitrarily. It is proposed that some interim solutions will be investigated but it is also considered necessary to conduct parallel fundamental studies to improve our understanding of the problem and hopefully define it in its simplest terms. It is recognized that many forms of dendrites can be propagated and that these forms depend largely on rates of charge and discharge.

The cycle life of a cell will be maximized by:

- (1) minimizing the depth of charge,
- (2) minimizing the rate of charge -- practices which are already observed.

It is recommended that in view of the observed "edge effects", failed cells should be subjected to post-mortem analysis to determine whether this is an attributable cause of failure. If so, consideration should be given to eliminating the side reservoir of electrolyte. Similar investigation of "end anodes" is recommended to determine whether growth on the rear surfaces is significant.

Some practical re-evaluation of the cellophane wrapping is needed to determine whether adequate zincate reservoirs are being provided within the negative envelope. Present configurations should be analyzed from this point of view and also to determine whether the cellophane envelope is wrapped in such a way that it does not allow preferred diffusion paths for the zincate through which dendrites will most readily propagate.

Some observations of local dendrite densification from cycle to cycle as a function of the depth of discharge are needed to determine the practical significance of this effect.

It is believed that some preliminary investigations of possible remedies can now be investigated. Initially this will be restricted to electrolyte modifications and modifications of the charging cycle.

Such a parallel program should lead to both short-term and long-term answers to the problem.